

Effect of anode and cathode flow field depths on the performance of liquid feed direct methanol fuel cells (DMFCs)

Rajavel Vijayakumar · Murugesan Rajkumar ·
Parthasarathi Sridhar · Sethuraman Pitchumani

Received: 24 November 2011 / Accepted: 18 February 2012 / Published online: 4 March 2012
© Springer Science+Business Media B.V. 2012

Abstract The effect of the anode and cathode flow field depths on the performance of a single cell Direct methanol fuel cell (DMFC) of 45 cm² active area were experimentally investigated. Double serpentine flow fields (DSFFs) with varying channel depth namely, 0.2, 0.4, 0.6, 0.8, and 1 mm but with fixed channel and rib width each of 1 mm on both anode and cathode were designed, fabricated, and tested. The experimental study involved measurement of pressure drops across anode and cathode flow field plates, polarization, and carbon dioxide concentration measurements at various current densities. The mass transport at both anode and cathode were found to increase with increase in pressure drop across the flow field on account of reduced channel depth from 1.0 to 0.4 mm at all current densities. However, further decrease to a channel depth of 0.2 mm was found to be counter-productive with different phenomena operating on either side viz., increased CO₂ slug length on the anode flow channel and increased methanol crossover on the cathode side. Hence, the maximum performance for DMFCs was observed for a channel depth of 0.4 mm on anode and cathode flow fields. A decrease in flow field channel depth at cathode was found to increase the methanol crossover due to convective mass transfer effect.

Keywords Direct methanol fuel cell (DMFC) · Flow field channel depth · Reynolds number · Hydraulic diameter · Pressure drop · CO₂ concentration (ppm)

1 Introduction

Direct methanol fuel cells (DMFCs) are potential power sources for numerous applications like laptops, mobile phones, and digital camera chargers due to system simplicity, high energy density (6,100 Wh kg⁻¹) of liquid fuel and easy refueling. Moreover, methanol is relatively inexpensive, easily stored and handled [1–4]. Methanol is oxidized along with water at anode of the DMFCs producing carbon dioxide (CO₂), electrons, and protons. In general, DMFCs use perfluorosulfonic acid-based Nafion membrane as electrolyte. Methanol readily transports across the Nafion membrane due to methanol crossover or methanol permeation. Methanol crossover causes mixed potential resulting in lowering of cell voltage, lowering of fuel and system efficiency. In a DMFC, the functions of anode and cathode flow field are supply and distribution of methanol solution and air, respectively, to the electrodes [5–12]. The distribution of the fuel on the electrode surface should ideally be as uniform as possible to ensure a uniform performance across the electrode surface. Anode flow field allows the methanol solution to permeate normal to its surface to the reaction layer, i.e., catalyst layer through Gas diffusion layer (GDL). Another function of the anode flow field of a DMFC is to transport CO₂ out of the cell. Wong et al. [13] investigated the effect of the geometry of the anode flow field plate on the performance. They reported that both shallower and deeper channel depth will lead to a reduction in the cell performance due to variation in liquid flow velocity. For the same flow rate of methanol, the liquid velocity increases with decrease in the channel depth, concurrently the increase in mass transport increases the performance of the cell. Yang and Zhao [14] concluded that the DMFCs with single serpentine flow fields (SSFF) demonstrated better performance than those with the

R. Vijayakumar · M. Rajkumar · P. Sridhar (✉) ·
S. Pitchumani
Central Electrochemical Research Institute, Chennai,
Tamil Nadu, India
e-mail: psridhar@csircmc.res.in

parallel flow fields (PFF). Lu et al. [15] experimentally conducted the effect of flow fields of various designs namely, double serpentine, single serpentine, mixed multichannel serpentine with wide, and narrow channels on the performance of micro-DMFCs. The results showed that DSFF with a channel depth of 0.3 mm gave higher performance than those with other channel depths due to increase in mass transport of methanol solution to electrode, and reported that single-channel serpentine design caused a slow response for changing electric load and took a long time to uniformly distribute the methanol solution over the entire active area of MEA.

Hwanga and Joha [16] research group also examined the performance of DMFCs by varying the cathode channel depth and got similar results and concluded that 0.3 mm channel exhibits higher performance than other channel depths because of the improved mass transport due to increase in pressure drop. Therefore, the mass transport of reactants is directly proportional to the pressure drop across inlet and outlet of the cell. Most of the reported literature is on the effect of flow field depth on either anode or cathode plate on the performance of DMFCs. However, to the best of our knowledge, this study is first of its kind to understand the influence of the depth of the channel on anode and cathode flow field together on the performance of DMFCs.

In this article, we present the effect of varying channel depth namely, 0.2, 0.4, 0.6, 0.8, and 1.0 mm on both anode and cathode flow field on the performance of DMFCs. Polarization (I–V), pressure drop and CO₂ concentration measurements are deployed for the above.

2 Experimental

2.1 Fabrication and assembly of DMFC single cell

The DMFC single cell designed and fabricated for this study is shown in (Fig. 1). It consisted of a membrane electrode assembly (MEA) sandwiched between two engraved anode and cathode graphite flow field plates, which were clamped with two aluminum fixtures. The electrodes of dimension $7.1 \times 7.1 \text{ cm}^2$ procured from M/s Johnson Matthey used in this study had 4 mg cm^{-2} loading of carbon-supported 1:1 Pt/Ru catalyst on the anode and 2 mg cm^{-2} loading of carbon-supported Pt on the cathode. The pre-treatment of Nafion® 117 membrane involved the following procedure: (1) boiling the membrane in 5 wt% H₂O₂ solution at 80 °C for 1 h, (2) rinsing with DI water at 80 °C for 1 h, (3) boiling the membrane in 0.5 M H₂SO₄ solution at 80 °C for 1 h, and (4) again rinsing with DI water at 80 °C for 1 h. Finally, the MEA was formed by hot pressing the assembly comprising membrane

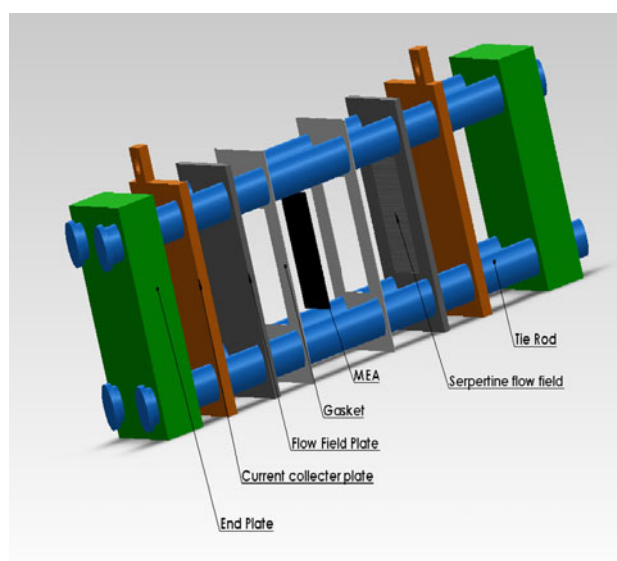


Fig. 1 Schematic view of fabricated in-house DMFC single cell

sandwiched between anode and cathode at 130 °C and 60 kg cm^{-2} for 3 min.

2.2 Design of flow field plate

Figure 2 shows the image of the flow field plate. Anode and cathode flow field graphite plates with two-serpentine channels of dimensions $1 \times 1 \text{ mm}^2$ (rib width \times channel width) and channel depths of 0.2, 0.4, 0.6, 0.8, and 1.0 mm

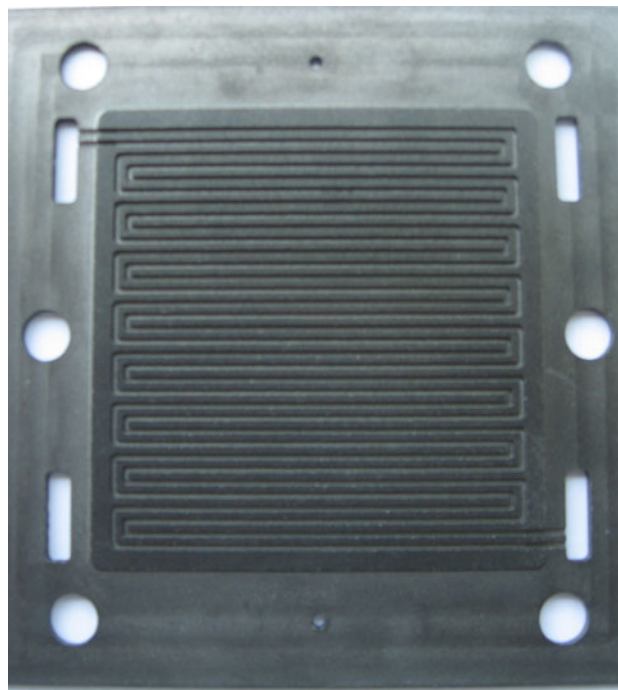


Fig. 2 Image of the flow field design

Table 1 Geometry of flow field plates

	Channel depth (mm)				
Anode	0.2	0.4	0.6	0.8	1.0
Cathode	0.2	0.4	0.6	0.8	1.0
Hydraulic diameter (D_h mm)	0.33	0.57	0.75	0.89	1.0
Reynolds number (N_{Re}) at ambient temperature					
Anode Re at 4 ml/min (methanol)	216.2	185.3	162.1	144.1	129.7
Cathode Re at 600 ml/min (Air)	1073.3	920	805.6	716	644.5
Rib and channel width 1 mm for all plates					

were designed and machined. A step of dimension ($10 \times 100 \times 0.53$ mm) was machined on the periphery of the flow field plate to seat the molded silicone gaskets. The open ratio of the channel to rib is 51% for all the flow field plates. Preliminary performance evaluation of DMFCs was conducted with flow field plates having the same channel depth for example 0.2, 0.4, 0.6, 0.8, and 1.0 mm on both the anode and cathode flow field plates. Reynolds number (N_{Re}) for different channel depths is calculated and listed in Table 1. The Reynolds number is the most important dimensionless number in fluid flow to define the flow characteristics. The Reynolds number is as given in Eq. 1,

$$N_{Re} = \rho V D_h / \mu \quad (1)$$

where V is velocity of the fluid in m s^{-1} , D_h is hydraulic diameter of the rectangular channel in m, ρ is the density of methanol or air in kg m^{-3} , and μ is the dynamic viscosity of methanol or air in $\text{kg m}^{-1} \text{s}^{-1}$. Density of 1 M aqueous methanol (992.41 kg m^{-3}) was measured by using the density meter (Mettler Toledo). Density of air at ambient temperature was taken as 1.116 kg m^{-3} . Velocity of the fluid was calculated from the pressure drop values using the Hagen–Poisuille Eq. 2.

$$\Delta P = 32 \mu L V / D_h^2 \quad (2)$$

in which D_h is the calculated using the following Eq. 3.

$$D_h = 2wh / (w + h) \quad (3)$$

where w is width of the channel, h is depth of the channel, and μ values for air are obtained from the literature [17].

2.3 DMFC test set up and testing conditions

All testings were carried out using Arbin instruments (FCT-158541) and the operating parameters were controlled with a computer. 1 M aqueous methanol solution was pumped from a reservoir using peristaltic (FMI Q) pump to the bottom inlet port on the anode and dry air from the cylinder through a mass flow meter (Bronkhorst) was connected to the top inlet port on the cathode to avoid flooding. The flow rate of 1 M aqueous methanol solution and air were kept at 4 ml min^{-1} and 0.6 Standard litre per

minute (SLPM), respectively. Cathode outlet port was connected to the carbon dioxide sensor (Vaisala CO_2 sensor M170) and pressure transducers (Honeywell Sensotec Sensors) were connected at the inlet of anode and cathode of the DMFCs. The DMFC single-cell test was carried out under ambient condition. The pressure drop and concentration of CO_2 (in ppm) were measured for DMFCs comprising anode and cathode flow field plates with varying channel depths at various current densities. 1 M methanol solution and air were circulated to the cell for 10 min to reach the steady state condition. The polarization curves were obtained in potentiostatic mode using fuel cell test station.

3 Results and discussion

3.1 Single cell polarization and performance comparison

Figure 3 shows the effect of varying channel depth namely, 0.2–1.0 mm on anode and cathode flow field plates on the performance of DMFC single cell. The Reynolds number corresponding to different channel depths at flow rates of

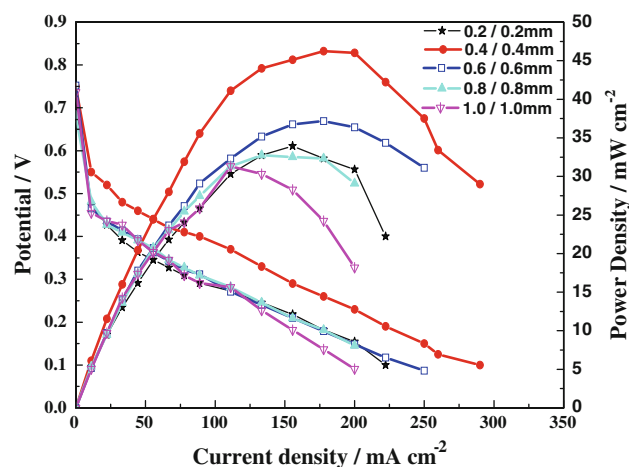


Fig. 3 Effect of varying flow channel depth on the performance of DMFCs with 1 M methanol and air at a flow rate of 4 ml min^{-1} and 0.6 SLPM at anode and cathode, respectively

4 ml min⁻¹ and 0.6 SLPM for 1 M methanol and air, respectively, are listed in Table 1. It is clearly seen from Fig. 3 that the maximum performance is obtained with DMFC comprising anode and cathode flow field plates having a channel depth of 0.4 mm, which is primarily attributed to the fact that for the same flow rates of methanol solution and air, the corresponding Reynolds numbers, 185.3 and 920, respectively are much higher compared to 162.1 and 805.6, 144.1 and 716, and 129 and 644.5 for those with corresponding channel depths of 0.6, 0.8, and 1.0 mm, respectively. Higher liquid/air velocity enhances the mass transfer from the flow channel to the GDL, thereby improving the cell performance [18, 19]. A further reduction in channel depth from 0.4 to 0.2 mm, however, causes the performance to decrease. This deviation can be explained as follows. For a given current, the volume of CO₂ produced is the same irrespective of the depth of the channel on the anode flow field plate. Anode flow field plates with shallower channel depths have less liquid flow volume and high CO₂ gas void fraction in flow channels. Gas void fraction increases along the channel length and the liquid flow can never be fully developed. Hence, the longer gas slugs in flow channels with smaller depth causes lowering of mass transfer from the channels. Thus, the DMFCs with 0.4/0.4 mm channel depth on the anode and cathode flow field plates exhibited a peak power density of around 47 mW cm⁻², which is the best performance among the entire flow field plates with varying depths of the channels tested. The above results on the channel depth effect indicate that there exists an optimal channel depth for the same channel width and the same open ratio when the flow rates of methanol and air are kept constant.

To optimize the performance of DMFC with respect to channel depth on the cathode side, the channel depth on the anode side is kept at 0.4 mm while the channel depth on the cathode side is varied from 0.2 to 1.0 mm and the results are presented in (Fig. 4). The maximum power density of 47 mW cm⁻² is observed for cathode flow field plate with a channel depth of 0.4 mm compared to those with channel depths of 0.6, 0.8, and 1.0 mm which is expected based on the Reynolds number as explained earlier. The deviation in performance for DMFC comprising cathode flow field plate with a channel depth 0.2 mm is due to increased methanol crossover that will be discussed later.

3.2 CO₂ measurement

Figure 5a illustrates the total concentration of CO₂ (cathode) measured at cathode side which is due to the CO₂ that crossed over from the anode to the cathode and that due to oxidation of crossed over methanol. Figure 5b illustrates crossed over CO_{2(crossover)} from the anode to the cathode

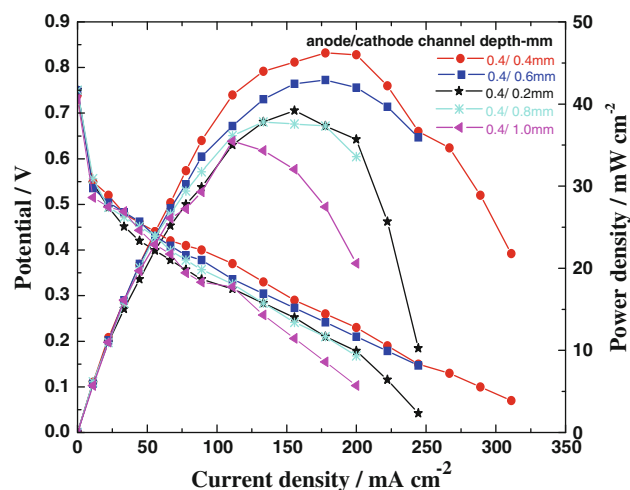


Fig. 4 Effect of varying cathode flow channel depth for a fixed anode channel depth of 0.4 mm on the performance of DMFCs with 1 M methanol and air at a flow rate 4 ml min⁻¹ and 0.6 SLPM at anode and cathode, respectively, under ambient conditions

and measured at cathode using 1 M methanol solution at anode and pure hydrogen at cathode and Fig. 5c illustrates the concentration of CO₂ (total—crossover), i.e., due to the oxidation of methanol that crossed over after accounting for CO₂ that crossed over from anode through the membrane. It is clearly seen from Fig. 5c that with decrease in channel depth, the methanol crossover increases at all current densities. At higher current densities the methanol concentration at the interface between the electrolyte membrane and the anode catalyst layer is lower resulting in decrease in methanol crossover. In order to understand the effect of channel depth on methanol crossover at various current densities, pressure drop measurements are conducted.

3.3 Pressure drop measurement

The mass transport is directly proportional to the pressure drop of the reactant between inlet and outlet of the cell. Hence, the pressure drop affects the performance of DMFC depending upon flow field design pattern, in particular, flow channel depth. Typical measured pressure drop across anode flow field plates by keeping the same channel depth on anode and cathode side while varying the current densities is given in Fig. 6a. A similar plot for the pressure drop across the cathode flow field plate is given in Fig. 6b. It is clearly seen from both the figures that the pressure drop increases with increasing current density. It is noteworthy that initially at lower current density (0–50 mA cm⁻²) the pressure drop across both anode and cathode increases to a maximum. Thereafter with increasing current density from 100 to 200 mA cm⁻², the pressure drop is almost constant for various channel depths. This behavior

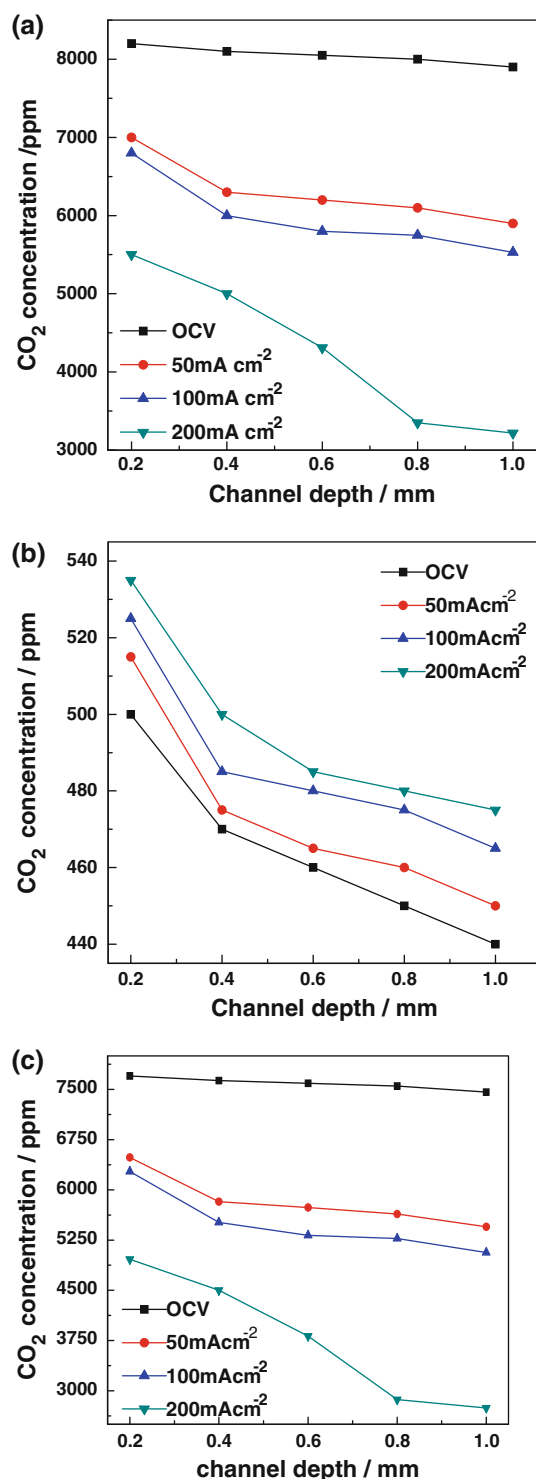


Fig. 5 Concentration of CO₂ (ppm) measured at cathode of DMFCs operating with 1 M methanol and air at a flow rate 4 ml min⁻¹ and 0.6 SLPM on the anode and cathode, respectively, at varying current densities and flow channel depths. **a** Total CO₂(cathode) (ppm), **b** crossover CO₂(crossover) (ppm) measured at cathode of DMFCs operating with 1 M methanol solution at anode and pure hydrogen at cathode, **c** concentration of CO₂ due to methanol crossover after accounting for crossover of CO₂ from anode to cathode

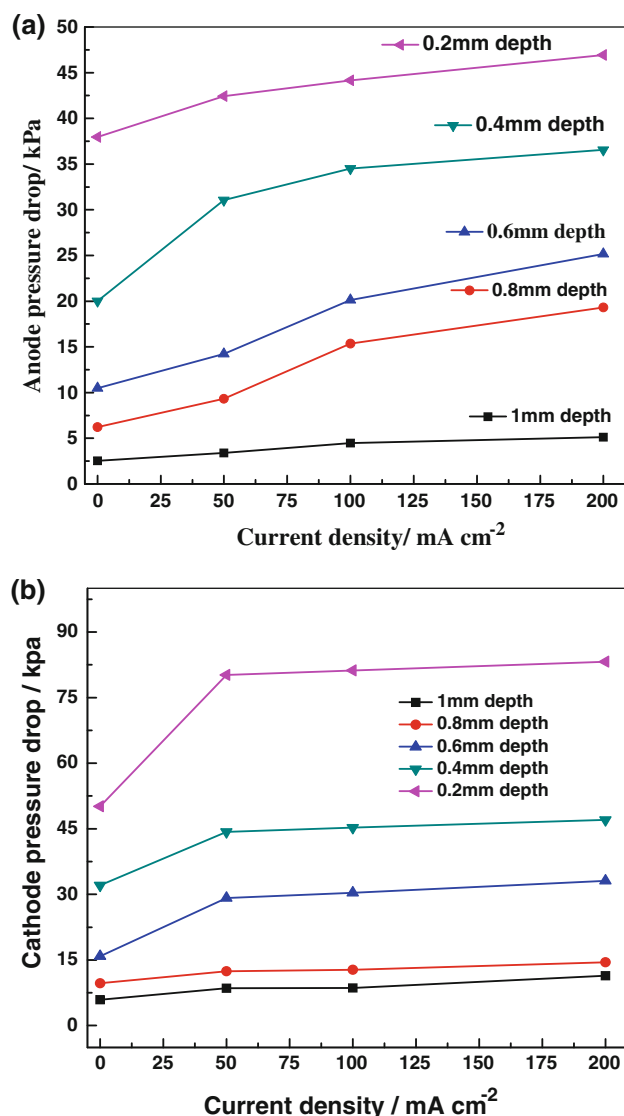


Fig. 6 Pressure drop measured for varying flow channel depth at **a** anode and **b** cathode as a function of current density

is similar to that observed by Buie Cullen and Juan Santiago [20] on the anode side and accounted for the liquid phase friction loss which is maximum at lower current densities, and the pressure drop reaches plateau as more gaseous CO₂ is evolved at higher current densities. As expected the pressure drop increase on the cathode side is comparatively lower since it contains almost single gaseous phase and low frictional losses than liquid methanol [21].

It is clearly seen that two contrasting effects namely, methanol crossover and pressure drop are operating for cathode flow field plates with a channel depth of 0.2 mm. The methanol crossover rate is the maximum which adversely affects the performance of DMFC while the maximum pressure drop is favorable for improved

performance. However, the former effect outweighs the latter resulting in overall decreased performance for DMFC comprising anode and cathode plates with a channel depth of 0.2 mm. The higher methanol crossover observed for cathode flow field plate with a channel depth of 0.2 mm could be due to convective mass transfer effect considering the fact that the aqueous methanol solution is separated by the membrane electrolyte from dry air that is circulated on the cathode side.

4 Conclusions

A maximum peak power density of 47 mW cm^{-2} is obtained for a flow field channel depth of 0.4 mm on both the anode and the cathode at ambient temperature. With increase in the depth of the flow field channel on both the sides, the pressure drop is found to decrease resulting in decreased performance. With decrease in the depth of the flow field channel to 0.2 mm on both the sides, the performance decreases due to increased methanol crossover and CO_2 gas void fraction.

Acknowledgments Financial support from CSIR, New Delhi, through a Supra Institutional Project under the Eleventh Five Year Plan is gratefully acknowledged. R.Vijayakumar is grateful to CSIR, New Delhi, for a Senior Research Fellowship.

References

1. Amphlett JC, Peppley BA, Ela H, Aamir S (2001) *J Power Sources* 96:204
2. Lu GQ, Wang CY (2004) *J Power Sources* 134:33
3. Dillon R, Srinivasan S, Arico AS, Antonucci V (2004) *J Power Sources* 127:112
4. Scott K, Argyropoulos P, Yiannopoulos P, Taama WM (2001) *J Appl Electrochem* 31:823
5. Yang WM, Chou SK, Shu C (2007) *J Power Sources* 164:549
6. Chen R, Zhao TS (2007) *Electrochim Acta* 52:4317
7. Xu C, Zhao TS (2007) *Electrochem Commun* 9:497
8. Jung GB, Su A, Tu CH, Weng FB, Chan SH (2007) *J Fuel Cell Sci Technol* 4:365
9. Arisetty S, Prasad AK, Advani SG (2007) *J Power Sources* 165:49
10. Gu Izow E, Kaz T, Reissner R, Sander (2002) *J Power Sources* 105:261
11. Liu WP, Wang CY (2007) *J Power Sources* 164:189
12. Jung GB, Su A, Tu CH, Lin YT, Weng FB, Chan SH (2007) *J Power Sources* 71(1):212
13. Wong CW, Zhao TS, Ye Q, Liu JG (2006) *J Power Sources* 155:291
14. Yang H, Zhao TS (2005) *Electrochim Acta* 50:3243
15. Lu Y, Reddy Ramana G (2011) *Int J Hydrogen Energy* 36:822
16. Hwanga SY, Joha HI (2008) *J Power Sources* 183:226
17. http://www.engineeringtoolbox.com/air-properties-d_156.html
18. Yang H, Zhao TS, Ye Q (2004) *Electrochem Commun* 6:1098
19. Cha SW, O'Hayre R, Lee SJ, Saito Y, Prinz FB (2004) *J Electrochem Soc* 151(11):A1856
20. Buie Cullen R, Juan Santiago G (2009) *J Heat Mass Transf* 52:5158
21. Argyropoulos P, Scott K, Taama WM (1999) *J Chem Eng* 73:217